COATINGS. ENAMELS

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PRODUCTION AND OPTICAL CHARACTERISTICS OF FILMS BASED ON ZIRCONIUM, YTTRIUM, AND IRON OXIDES

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The effect of the composition of film-forming solutions on the optical characteristics of films in the $(0.92ZrO_2 \cdot 0.08Y_2O_3) – Fe_2O_3$ system is considered. The kinetics of this process is discussed.

Thin films based on zirconium dioxide find wide application due to their high optical parameters and increased chemical and mechanical resistance. Zirconium dioxide is transparent in the ultraviolet (over 200 nm, of forbidden-band width about 6 eV), visible, and near infrared spectrum ranges. To prevent volume inversions of ZrO_2, it is transformed into a stable high-temperature modification by introducing additives of structurally similar oxides that form stable solid solutions with a face-centered cubic lattice (f.c.c.). Yttrium oxide is the most promising stabilizer [1]. Complete stabilization of the f.c.c. structure of ZrO_2 occurs on introducing 8% Y_2O_3 (here and elsewhere molar content).

For deliberate modification of the optical properties of such films, for instance, decreased transmission in the UV and visible spectrum ranges, it is necessary to introduce oxides of transition metals absorbing in the specified spectrum range. Such additive selected for the present study was iron (III) oxide. Solid solutions of compositions $0.92ZrO_2 \cdot 0.08Y_2O_3$ and Fe_2O_3 act as components of the pseudobinary system $(ZrO_2 \cdot 0.08Y_2O_3) – Fe_2O_3$. The use of stabilized ZrO_2 as one of the components makes it possible to expand the stability range of the f.c.c. of the solid solution compared with the $ZrO_2 – Fe_2O_3$ system [2] and to control more smoothly the film properties.

The purpose of our study was to investigate the effect of the synthesis conditions on the phase composition and optical characteristics of thin-film materials of the $(0.92ZrO_2 \cdot 0.08Y_2O_3) – Fe_2O_3$ system.

The film-forming solutions (FFS) were obtained using zirconium oxychloride octahydrate, iron chloride hexahydrate, and yttrium chloride hexahydrate. The total content of the initial salts (converted to oxides) in the FFS was 0.4 M. The component ratio (converted to oxides) was: $ZrO_2 : Y_2O_3 = 0.92 : 0.08\%$; Fe_2O_3 (in ratio to $ZrO_2 + Y_2O_3$) = 0 – 100%.

The solvent was ethyl alcohol rectificate that was preliminarily redistilled and dried by boiling with CaO.

The films were applied to substrates of glass, quartz, monocrystalline silicon, and polycor. The substrates were held in a chromium mixture, washed with distilled water, then dried. The films were obtained by centrifuging at 1000 – 5000 min^{-1}.

The structure and optical characteristics of oxide sol-gel films depend on many factors: on the FFS composition, its viscosity, surface tension, temperature, rotational speed, and moisture [3]. To simplify the study of the effect of the synthesis parameters on film properties, we carried out a factorial experiment. The selected factors were the molar content of Fe_2O_3 X_1 and the rotational speed of the centrifuge X_2. The response function Y was the refractive index of the films on glass substrates. The refractive index and thickness were determined using a LÉF-3M laser ellipsometer (wavelength 632.8 nm). The experiment was designed in two areas of the factor space.

The first model was constructed in the interval of Fe_2O_3 content of 0 – 50% and the rotational speed of the centrifuge 1000 – 3000 min^{-1}. The model has the following form:

$$Y = 1.903 – 1.32 \times 10^{-1} X_1 + 3.44 \times 10^{-2} X_2 + 4.85 \times 10^{-2} X_1X_2.$$

An analysis of the model indicated that the Fe_2O_3 content has the greatest effect and, as it decreases, the refraction index of films increases. Introduction of iron chloride intensifies the hydrolysis of zirconium oxychloride and increases the size of the globules of hydroxyzirconium and iron hy-

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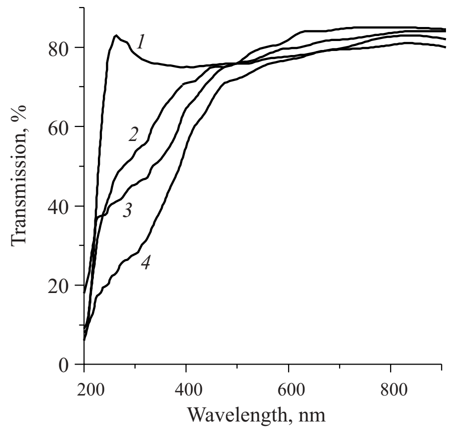

Fig. 1. Transmission spectra of $(0.92ZrO_2 - 0.08Y_2O_3)_{1-x}(Fe_2O_3)_x$ films on quartz substrates: *1*, *2*, *3*, and *4*) $x = 0$, 0.125, 0.375, and 0.5, respectively.

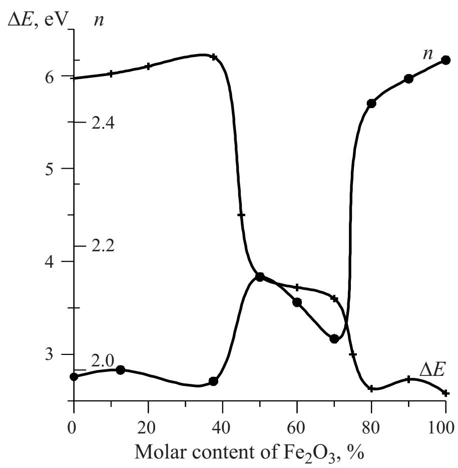

Fig. 2. Composition – property diagrams of films in the $(0.92ZrO_2 \cdot 0.08Y_2O_3) - Fe_2O_3$ system.

drate in the FFS [2]. This contributes to the formation of a film with elevated porosity. At the same time, with increasing rotational speed, the refractive index grows, which is related to the condensation of the film under the centrifugal force effect in the rotation of the substrate.

The second model is calculated for the Fe_2O_3 content in the interval of 0 – 50% and the rotational speed of 3000 – 5000 min^{-1}.

$$Y = 1.972 - 5.906 \times 10^{-2} X_1 + 3.99 \times 10^{-2} X_2 + 2.23 \times 10^{-2} X_1 X_2.$$

The effect of the factors on the refractive index in this range on the whole does not differ from the previous range. However, the effect of X_1 on this parameter is less significant. The refractive index of the films is higher in this range.

To obtain films with a high refractive index, a rotational speed from 3000 to 5000 min^{-1} as used. At the same time, the content of iron chloride in the FFS and the rotational speed in deposition on the substrate were increased.

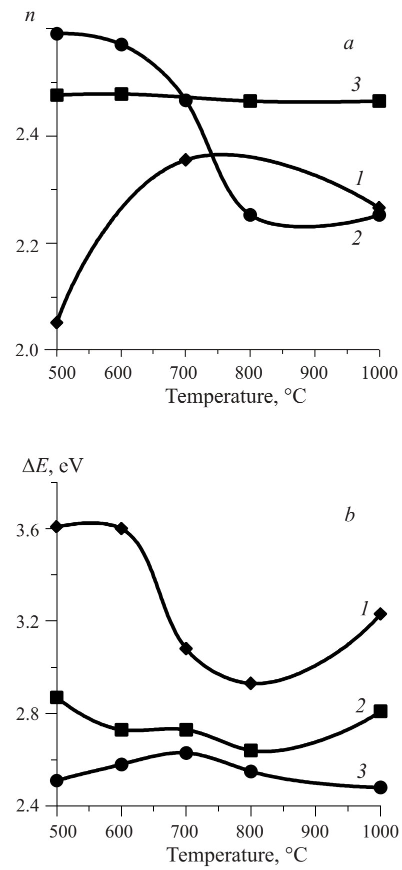

Fig. 3. Effect of heat-treatment temperature on the refractive index n (*a*) and forbidden-band width ΔE (*b*) of films in $(0.08Y_2O_3 \cdot 0.92ZrO_2)_{1-x}(Fe_2O_3)_x$ system: *1*, *2* and *3*) $x = 0.7$, 0.9, and 1.0, respectively.

The films were heat-treated in a drying cabinet at a temperature of 150°C and then in a muffle furnace at 500 – 1000°C.

The heat treatment conditions for the films of the ternary system was selected based on the data earlier obtained by us for a binary system [1, 2, 4].

The resulting films are homogeneous, transparent, and have high adhesion to glass, quartz, monocrystalline silicon, and polycor. A study of transmission spectra of films on quartz substrates in the visible and UV spectrum ranges (using a Specord M40 spectrophotometer) demonstrated that an increase in the iron oxide content in the FFS increases the absorption in the UV and the visible spectrum range, and the transmission edge is shifted to the long-wave range (Fig. 1). The yellow-brown color of the films is intensified. The forbidden-band width calculated based on the electron spectra according to the absorption edge wavelength decreases.

The dependences of the refractive index of films on polycor substrates and of the forbidden-band width of films on quartz substrates on their compositions was investigated (Fig. 2). The diagram can be arbitrarily split into three seg-

ments, inside which the specified characteristics vary regularly: 0 – 40, 40 – 70, and 70 – 100% Fe_2O_3. The x-ray phase analysis data (DRON-3, CuK_α radiation) indicate that with an Fe_2O_3 content equal to 0 – 40%, a solid solution is formed on the basis of the f.c.c. modification of ZrO_2, and with Fe_2O_3 equal to 40 – 70 and 70 – 100%, solid solutions are formed on the basis of ferrous oxide. Zirconium dioxide in these ranges exists in the amorphous form. The x-ray pattern exhibits blurred peaks correlating with the most intense reflections of the f.c.c. lattice of Zr_2O. As the content of ZrO_2 in the system decreases, the degree of crystallinity of this phase grows, the intensity of its reflections increases, and their half-width decreases. The variations in the refractive indexes and the width of the forbidden zone of films depending on their composition agrees with the phase composition variation.

An increase in the heat treatment temperature of $ZrO_2 - Y_2O_3$ and Fe_2O_3 films up to 1000°C has virtually no effect on the forbidden-band width and the refractive index. The insignificant increase in the refractive index and a certain decrease in the forbidden-band width may be due to recrystallization of the film. Heat treatment of films of the $(0.92ZrO_2 \cdot 0.08Y_2O_3) - Fe_2O_3$ system at 500 – 1000°C leads to intensifying the typical reddish-brown tint of ferrous oxide and changes the refractive index and the forbidden-band width (Fig. 3). The x-ray phase analysis shows that the degree of crystallinity of ZrO_2 and Fe_2O_3 phases in the system grows and their reflections shift. This shows that certain processes occur in the solid phase that lead to a redistribution of the components between ZrO_2 and Fe_2O_3. Consequently, the resulting solid solutions are metastable and with increasing heat-treatment temperature they disintegrate.

Thus, films of the $(0.92ZrO_2 \cdot 0.08Y_2O_3) - Fe_2O_3$ system with a high refractive index (2.0 – 2.6) and a forbidden-band width of 2.4 – 6.0 eV are obtained from film-forming solutions based on ethyl alcohol, zirconium oxychloride, and yttrium and iron oxides.

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